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Post-Processing Method for Polyvinyl Alcohol-Based Synthetic Fiber and Other Molded Articles

Detailed Description of the Invention

It is known to attain an object of obtaining a polyvinyl alcohol-based synthetic fiber and other molded articles that are excellent in hot water resistance, particularly in elasticity, by introducing a side chain having a great steric barrier effect into an amorphous part of polyvinyl alcohol with the use of higher aldehyde.

Aldehyde having 4 or more carbon atoms is an effective treatment agent for such object, but such aldehyde becomes hardly soluble to water along with an increase in number of carbons, thereby making it gradually difficult to cause a reaction only by using water. In general, as can be seen in Patent No. 159969, a large amount of lower alcohol such as methyl alcohol and ethyl alcohol is used for acetalizing such hardly soluble aldehyde, or, as can be seen in Patent No. 208458, a reaction is caused by way of emulsifying dispersion or solubilization with the use of a surfactant.

However, such methods have a drawback that it gradually becomes difficult to perform the treatment when the solubility of aldehyde to water at an ordinary temperature is 0.2% or less.

That is, since the lower alcohol such as methyl alcohol and ethyl alcohol has a low boiling point and that solubility of higher aldehyde is small, a larger amount of methyl alcohol or ethyl alcohol is required for dissolving aldehyde required for the reaction. However, the increase in methyl alcohol or ethyl alcohol considerably lowers a reaction speed, thereby raising a drawback that an increase in reaction speed achieved by the increase in aldehyde concentration is cancelled out. Also, in the method of treating in emulsifying dispersion state, stability of an emulsion liquid tends to be deteriorated to make it difficult to perform uniform reaction. Therefore, the acetalization with higher aldehyde having solubility to water at an ordinary temperature of 0.2% or less has heretofore been a considerably difficult problem and is hardly ever performed.

As a result of various studies conducted by the inventors in order to industrially and more advantageously perform the acetalization with the use of hardly soluble higher aldehydes, the inventors succeeded in achieving a greater reaction in a short time by using n-propyl alcohol and iso-propyl alcohol as compared to the conventional case of using methanol and ethanol, and, in the case of industrial acetalization with the use of hardly soluble aldehyde, it is possible to achieve a greater reaction in a short time as compared to the case of using methanol and ethanol. The effect is considerably prominent, and a difference between methanol/ethanol and

propanol is considerably great, and butanol enables a further reduction as compared to propanol. As described above, the inventors found that the effect of propanol is considerably peculiar and that propanol exhibits the special effect that makes it difficult to simply consider propanol as a homologous compound of methanol and ethanol.

This invention is characterized by a treatment method for a polyvinyl alcohol-based synthetic fiber and other molded articles with acetalizing higher aldehyde that is hardly soluble or insoluble to water by using n-propyl alcohol or iso-propyl alcohol in a system in which 10% or more of water is present.

Boiling points of n-propyl alcohol and isopropyl alcohol are 97.2°C and 82.4°C under an ordinary pressure, which are higher than those of methyl alcohol and ethyl alcohol, and such boiling points indicates an advantage of enabling treatment of a fiber at a higher temperature.

Also, properties of n-propyl alcohol and iso-propyl alcohol of dissolving higher aldehyde in the presence of water are far more excellent than those of methyl alcohol and ethyl alcohol under the same conditions, and such properties indicate capability of an acetalization reaction with the use of alcohol having a lower concentration and enables a considerably great advantage of increasing a reaction speed.

In contrast, higher alcohol such as butyl alcohol has

a low solubility to water, and it is difficult to use such alcohol as a solvent for the acetalization reaction. As to solubility to water at an ordinary temperature, n-butyl alcohol has 9% of solubility, secondary butyl alcohol has 12% of solubility, iso-butyl alcohol has 10% of solubility, n-amyl alcohol has 27% of solubility, and iso-amyl alcohol has about 28% of solubility, and it is impossible to dissolve higher aldehyde of a degree required for the reaction into such solutions.

The excellent solubility of higher aldehyde to n-propyl alcohol and iso-propyl alcohol can be explained as follows by using α-naphthaldehyde.

An aqueous solution having a n-propyl alcohol concentration of 20% or an aqueous solution having an iso-propyl alcohol concentration of 25% is sufficient for dissolving 1.56% of α-naphthaldehyde at 70°C, while it was confirmed that 40% of methyl alcohol concentration or 35% of ethyl alcohol concentration is required (in a tightly sealed container).

The above-mentioned fact is considerably important for treating the polyvinyl alcohol-based synthetic fiber and other molded articles with higher aldehyde, and this invention solves the conventional problem of the remarkable reduction in reaction speed caused by the higher concentration of methanol that is required for increasing the aldehyde

concentration for achieving a required degree of reaction in a treatment with higher aldehyde in a methanol system.

Further, it is difficult to increase a reaction temperature with the use of methyl alcohol or the like. Though it is possible to effectively perform the reaction with the use of benzaldehyde or the like that can react at a relatively low temperature, it is considerably difficult to increase the reaction temperature with the use of higher aldehyde such as naphthaldehyde, and industrial practice thereof has been considered difficult since it has been necessary to use a tightly sealed container for allowing the reaction at a high temperature. However, this invention overcomes such problems.

Results of a reaction using an alcohol aqueous solution having a constant concentration in performing acetalization with the use of naphthaldehyde are shown below. As the α-naphthaldehyde concentration, a concentration close to saturation was selected in each of the reaction conditions.

Type of alcohol	Alcohol concentration (%)	Sulfuric acid concentration (%)	α-naphthaldehyde concentration (%)	Temperature (°C)	Time (hr)	Acetalization degree (mol)%
-	0	5	0.05 *	70	2	0.5
-	"	"	" *	80	"	1.0
Methyl alcohol	25	"	0.7	70	"	8.3
"	"	"	0.1 **	60	"	1.0
"	40	"	0.7	60	"	6.6
Ethyl alcohol	25	"	0.5	70	"	7.0
"	40	"	2.8	"	"	1.8
Iso-propyl alcohol	25	"	1.5	"	"	2.0
"	"	"	"	75	"	2.5
"	90	"	"	70	"	0.7
n-propyl alcohol	25	"	1.9	70	"	2.6
"	"	"	2.3	80	"	2.8
"	90	"	1.9	70	"	0.9
n-butyl alcohol	7	"	0.2	"	"	1.5
"	"	"	0.3	80	"	2.5

* Dissolution was imperfect when naphthaldehyde was 0.05%, and acetalization was performed as it was.
** Dissolution was imperfect when naphthaldehyde was 0.1%, and acetalization was performed as it was.

As describe above, the use of n-propyl alcohol or iso-propyl alcohol achieves an advantage of enabling easy acetalization in the case of the treatment with the use of higher aldehyde.

However, in the case of using n-propyl alcohol or iso-propyl alcohol, when the concentration of n-propyl alcohol or iso-propyl alcohol in the acetalization bath is 90% which is high to cause the concentration of water to 10% or less, the reaction speed is remarkably reduced as shown in the table, and practicability in terms of operation is totally lost.

It is needless to mention that the great dissolution power and the high boiling point of n-propyl alcohol or isopropyl alcohol are effectively utilized particularly in the acetalization reaction with the use of aldehyde having solubility to water of 0.2% or less at an ordinary temperature, and it is considered that the great dissolution power and the high boiling point are industrially significant due to the advantage of enabling a treatment with the use of an alcohol solution having a lower concentration in the case of using aldehyde such as benzaldehyde having solubility of about 0.2% to 0.5% at a higher reaction temperature.

Each of n-propyl alcohol and iso-propyl alcohol may be used alone, but it is possible to use n-propyl alcohol or iso-propyl alcohol in combination with other organic substances such as methyl alcohol, ethyl alcohol, butyl

alcohol, dioxane, dimethylformamide, and dimethylsulfoxide.

It has been known that the acetalization occurs in a reaction system solely containing alcohol and not containing water, but a reaction speed in such reaction system is considerably low and requires industrially impracticable reaction condition which is several tens of hours and considerably undesirable as compared to the method of this invention. The reason for the necessity of at least 10% of water is that the reaction speed of hardly soluble aldehyde is considerably reduced when the water is less than 10%.

Hereinafter, examples will be described.

Example 1

A polyvinyl alcohol fiber that was obtained by wet spinning according to an ordinary method was subjected to a heat treatment under fixed length at 235°C in the air for 3 minutes. The fiber was reacted in an aqueous solution comprising 1.56% of α-naphthaldehyde, 5% of sulfuric acid, and 25% of iso-propyl alcohol at 70°C for 2 hours. An acetalization degree of the thus-obtained fiber was 20.3%, and the fiber exhibited a shrinkage ratio after being left in boiling water for 30 minutes of 5%. A tensile elasticity of the fiber was remarkably good.

Example 2

By using the fiber same as that of Example 1, α -naphthaldehyde was dissolved into an aqueous solution of 5%

of sulfuric acid and 40% of methyl alcohol until saturation, followed by a reaction at 60°C for 2 hours. An acetalization degree of the thus-obtained fiber was 6.3%, and the fiber exhibited a shrinkage ratio in boiling water of 20% or more.

A reaction was allowed for 2 hours in an aqueous solution comprising 1.56% of α-naphthaldehyde, 5% of sulfuric acid, and 40% of methyl alcohol (1.56% of α-naphthaldehyde with respect to 40% of methyl alcohol means an almost saturated concentration at 70°C) in a tightly sealed container at 70°C for 2 hours. An acetalization degree of the thus-obtained fiber was 16% (it was confirmed that 4.5 hours or more is required for achieving an acetalization degree of 20% or more under the above reaction conditions).

Example 3

By using the fiber same as that of Example 1, a treatment was performed in an aqueous solution comprising 1.56% of α-naphthaldehyde, 10% of H_2SO_4, and 20% of n-propyl alcohol at 80°C for one hour. An acetalization degree of the fiber was 21.2%, and the fiber exhibited good hot water resistance and elasticity.

Example 4

By using the fiber same as that of Example 1, a treatment was performed in an aqueous solution comprising 1.6% of 7-formyl-1,2,3,4- tetrahydronaphthaline, 5% of sulfuric acid, and 25% of iso-propyl alcohol at 70°C for one hour. An

acetalization degree of the fiber was 21.0%, and the fiber was resistant to boiling water and exhibited elasticity.

Example 5

A polyvinyl alcohol fiber obtained by dry spinning according to an ordinary method was drawn to about 4 times of its original length and subjected to a heat treatment under fixed length (at 220°C). The fiber was allowed to react in an aqueous solution comprising 1.8% of P-phenylbenzaldehyde, 10% of sulfuric acid, and 27% of n-propyl alcohol at 70°C for 4 hours. An acetalization degree of the fiber was 24%, and the fiber exhibited good hot water resistance and elasticity.

Example 6

Wet spinning was performed in accordance with an ordinary method by mixing, with untreated polyvinyl alcohol, polyvinyl alcohol that had been amino-acetalized with β-cyclohexylaminobutyl aldehyde. Drawing of 39%/5 seconds was performed at 235°C, and a heat treatment under fixed length was performed at 240°C for 5 seconds. The thus-obtained fiber was treated in an aqueous solution comprising 1% of benzaldehyde, 2% of sulfuric acid, and 10% of iso-propyl alcohol at 70°C for one hour. A benzalation degree of the fiber was 22%, and the fiber exhibited good hot water resistance, elasticity, and dye affinity.

Example 7

The heat treated fiber of the foregoing example was

treated in an aqueous solution comprising 1% of P-chlorbenzaldehyde, 2% of sulfuric acid, and 25% of n-propyl alcohol at 70°C for one hour. An acetalization degree of the fiber was 20%, and the fiber exhibited good hot water resistance, elasticity, and dye affinity.

Example 8

The fiber same as that of Example 1 was used, and a reaction was allowed in an aqueous solution comprising 2.0% of n-lauryl aldehyde, 10% of sulfuric acid, and 35% of n-propyl alcohol at 80°C for 2 hours. An acetalization degree of the fiber was 23%, and the fiber exhibited excellent elasticity.

Example 9

A polyvinyl alcohol film was brought into a tense state, and a heat treatment was performed at 230°C in the air for 5 minutes. The thus-obtained film was treated in an aqueous solution comprising 10% of sulfuric acid, 10% of β-naphthaldehyde, and 20% of iso-propyl alcohol at 60°C for 30 minutes, thereby obtaining a film having a high water repelling property.

Claim

A post-treatment method for a polyvinyl alcohol-based synthetic fiber and other molded articles, characterized by a treatment using n-propyl alcohol or iso-propyl alcohol in a system in which at least 10% or more of water is present when treating a polyvinyl alcohol-based synthetic fiber and other

molded articles with aldehyde that is hardly soluble or insoluble to water.